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(54) Title: CYANIDE CONTAINING EFFLUENT PURIFICATION PROCESS

(57) Abstract

An improved two-stage process for purifying cyanide-containing effluent. At the first treatement stage the effluent and microorganism culture in an amount between 0.6- to 1.0 g/l are introduced into a chamber, and the mixture is agitated by means of air for between 24 to 72 hours, at a temperature between 26 to 30 °C. At the second treatment stage said mixture of effluent and microorganism culture is further supplied to another chamber, containing the anion-exchange resin of gold selectivity between 0.4 to 1.2 l/m3, which was previously introduced thereinto, and the agitation of resultant mixture by means of air is performed for between 0.5 to 3.5 hours.

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CYANIDE CONTAINING EFFLUENT PURIFICATION PROCESS

The invention refers to a process for purifying cyanide-containing effluent typically emitted in gold-extracting plants, galvanic process plants, non-ferrous metallurgy plants, and the like.

The effluent of non-ferrous metallurgic and gold-recovery plants is the main source of contamination of water basins with cyanide compounds. The development of the efficient processes for decontaminating this effluent still remains an urgent task.

There have been proposed many physical and chemical methods for purifying effluent from cyanides. These methods are, however expensive and non-profitable. Moreover, the known processes adversely affect the environment due to the involvement of such toxic substances as liquid chlorine.

It is known the application of microorganisms in cyanide destruction of recycled water supply of metallurgy plants (Chmielowski S., Nowak-Rotsides E., Szwagiel M. --Pr.naul USL., Kotowicach Acta biol. Sites.- 1985, v.18, p.93-106)

The known methods of cyanide destruction involve the use of microorganisms which utilize cyanide-containing nitrogen compounds and carbon in their metabolism process.

Heterotrophic gram-negative bacteria are of utmost importance for cyanide destruction process. The researches have demonstrated the possibility of microorganism adoption to cyanides as well as the involvement of autotrophic and heterotrophic microorganism strains such as **Pseudomonas Bacillus genera** in cyanide destruction process.

The oxidation- and- reducion nature of cyanide transformation by microorganisms is also well known (Microbiology, 1977, v.46, N2 p.294-298).

Microorganisms capable of destructing cyanides are separated from the technogenic effluent of gold-recovery plants. The bacterial associations and some monocultures pertain to this group of microorganisms.

As a result of long-term adaptive selection of microorganisms to the increased cyanide concentrations, there were obtained the following most active microorganism strains: **Pseudomonas sp. 1; Pseudomonas aeruginosa A; Pseudomonas fluorescens B-5040 and Bacillus sp. T2** (S.V. Garbara, Z.R. Ulberg, N.I. Grischenko, V.I. Podolskaya, Microbiology Journal. - 1992, v. 54, N3, p.44-48).

There also exists a proof of sanitary safety of metabolites of microbial transformation of cyanides.

A number of technical solutions are known in the art relating to the treatment of cyanide-containing effluent by means of cyanide-destructing microorganisms.

For example, SU, A, N 637333 discloses a process for purifying effluent from cyanides by providing the treatment of waste water of pH between 7.0 to 8.5 by the mixture of heterotrophic microorganisms including **Bacterium liquefaciens, Bacterium album, Bacillus brevis, Pseudomonas flurescens.** Cyanide destruction occurs after 20 days of contact between the effluent and said mixture of microorganisms. The above process has the disadvantage in that it may be used only for treating effluent of low cyanide concentration (about 17.5 g/l) and of neutral or near neutral pH value. Besides, this process is rather time-consuming.

Another process for removing cyanides from the effluent is specified in a.c. CSSR N259127, wherein the **Fusarium moniliforme** microorganism culture in an amount between 0.01 to 10.0 g/l is added to the water, containing up to 50.0 mg/l of cyanides at a temperature between 15 to 25'C and at pH between 4.0 to 12.0. Cyanide destruction occurs after 120 hours. This process is likewise time-consuming and suitable only for treating effluent of low cyanide content.

Further prior art process of purifying effluent of up to 1000 mg/l of cyanides is recited in

Romania patent N 69528. According to this patent the inoculate of Scenedesmus microorganism strain in an amount between 1.4 to 2.0 g/l is introduced into the water to be treated. The cultivation of microorganisms is performed at a temperature between 20 to 25° C and at pH 10.0 over a period of 6 hours. Said process enables the concentration of cyanides contained in effluent to be reduced to 1.0 mg/l. So, the effluent subjected to purifying from cyanides still contains rather high concentration of cyanides, and needn't be discharged into the natural water streams because of negative impact on the environment. In all likelihood, in this case there were not removed the cyanides being present in the water in the form of heavily-destructed metal complexes. Moreover, said process cannot be used for the efficient purification of the effluent containing high concentration of suspended cyanides as well as of rhodanides.

Notably. after the cyanidation stage the effluent of gold-extracting plants and other production processes still contains a certain amount of dissolved gold and other noble metals. These metals are usually lost, because the known processes of effluent treatment do not involve the simultaneous extraction of valuable components, such as gold and silver, in a single process of water treatment.

The object of this invention is to increase the efficiency of purifying effluent from cyanides, with simultaneous extraction of dissolved noble metals in a single process of water treatment.

Further object of the invention is to improve the efficiency of removing cyanides from the effluent containing high concentration of cyanides in suspension.

In accordance with these and other objects of the invention a two-stage process for purifying effluent from cyanides is provided, consisting in that at the first treatment stage the

effluent and microorganism culture in an amount between 0.6 to 1.0 g/l are introduced into a chamber, and agitation of a mixture of effluent and microorganism culture is performed by means of air for a period between 24 to 72 hours; at the second treatment stage said mixture of effluent and microorganism culture is further introduced into a chamber, whereinto an anion-exchange resin of gold selectivity between 0.4 to 1.2 in an amount between 3.0 to 5.0 litres per cubic metre of effluent and microorganism culture is added, and the agitation of the resultant mixture by means of air is performed for between about 0.5 to about 3.0 hours.

The above two-stage process for purifying cyanide-containing effluent provides the unexpected effect of increasing the destructive capacity of microorganisms in relation to cyanides in the presence of both the disperse phase (i.e. liquid suspension) and anion-exchange resin. Agitation of the effluent and microorganism culture by air at the first stage beneficially influences the microorganism vital activity and, furthermore, contributes to the breakdown of cyanides in a suspended state. It appears that at the first stage the microorganism culture is immobilized on the disperse (suspended) cyanide particles surface, and with air agitation it is able to reproduce to a greater degree thereon which increases the destructive properties of microorganisms in relation to cyanides. Subsequently, at the second treatment stage the microorganisms are similarly immobilized on anion-exchange resin particles, which are also maintained in a suspended state when being agitated by air. The microorganism culture is growing on the anion-exchange resin particles and its destructive properties towards the cyanides are improved thereby. At the same time, the selective capacity of anion-exchange resin towards the gold or other effluent-dissolved noble metals is also utilized.

It is recommended that in a continuous process of effluent treatment the agitation of

effluent and microorganism culture by air at the first treatment stage be successively performed at least in two additional chambers. The time of agitation of said mixture in each of said chambers constitutes between 8 to 24 hours.

It is the most advisable that Ps. fluorescens B-5040 strain be used as microorganism culture, and agitation be carried out at a temperature of said effluent and microorganism culture mixture between 26 to 30°C. This embodiment of the invention provides the most efficient purification of effluent from cyanides as well as the highest rate of gold extraction.

Alternatively, at the first treatment stage, in the chamber containing the mixture of effluent and microorganism culture, an electric field of intensity between 0.5 to 2.0 V/cm can be utilized, and agitation of said mixture be performed within said electric field. This embodiment of the invention makes it possible to intensify the vital activity of microorganism cells resulting in a considerable improvement of effluent treatment under batch operation conditions.

It is preferred that an electric field of intensity between 0.5 to 2.0 V/cm be produced at least in two chambers where the agitation of said effluent and microorganism culture is performed, and the agitation of said mixture within said electric field be carried out at least in these two chambers. This embodiment of the invention allows to intensify the vital activity of microorganism cells and to considerably improve the process of water purification under continuous operation conditions.

According to further embodiment of the invention,an electric field of intensity between 0.5 to 2.0 V/cm can be produced at the first treatment stage, and the agitation of effluent and microorganism culture can be first performed within the electric field for about 30-60 sec., followed by further agitation of said mixture for between 0.25 to 1.0 hour without any electric field being applied. It should be stressed that such alteration of agitation by electric

field and without this field being applied must be performed during the whole period of agitation of said effluent and microorganism culture at the first treatment stage.

The above modification enables the vital activity of microorganism cells to be intensified, and results in considerably improved effluent purification under batch operating conditions, with the electric energy consumption to be simultaneously reduced.

According to further embodiment of the invention it is recommended that the electric field of intensity between 0.5 to 2.0 V/cm be produced in at least two chambers at the first treatment stage, and the agitation of effluent and microorganism mixture be performed for between 30 to 60 sec. within said electric field, with further agitation be carried out for between 0.25 to 1.0 hour without the application of said electric field. The above alteration of agitation of said mixture under the effect of electric field and without the application of this field must be maintained during the whole period of agitating said mixture of effluent and microorganism culture in each of said chambers. This embodiment of the invention permits to intensify the vital activity of microorganism cells resulting in the improvement of effluent treatment under the continuous operation conditions, as well as in the reduction of electric energy consumption.

It is also expedient to agitate the mixture of effluent and microorganism culture by air with the ratio of effluent and microorganism mixture to air being between 1:1 to 1:2 respectively. This modification of the invention makes it possible to efficiently oxygenate effluent, and advantageously influences the vital activity of microorganism cells.

In accordance with one more embodiment of the invention, as an anion - exchange resin there may be used the weak-based anion-exchange resin from styrene and divinylbenzene copolymer, containing 10% divinylbenzene and having the weak-based N(CH3)2 groups and strong-based N+(CH3)3 groups, with its gold selectivity value being 1.2. This embodiment

ensures the highest efficiency of gold extraction with simultaneous effective removal of cyanides from effluent in a treatment process.

Alternatively, the strong-based anion-exchange resin from styrene and divinyl - benzene copolymer, containing the strong-based N+(CH3)3 groups and having gold selectivity value of 0.5, may be also used to achieve the objects of the invention. This embodiment enables the efficient destruction of cyanides in the effluents of high rhodanide content, as well as allows the simultaneous recovery of noble metals from water.

It is recommended that prior to effluent supply to the first treatment stage it should be passed through **Pseudomonas fluorescens B-5040** microorganism culture immobilized on a solid carrier.

In case of strong increase of cyanide concentration in effluent to be purified such treatment permits to avoid the death of microbial cells, especially at the first treatment stage. Furthermore. due to intensive reproduction process, the immobilized microorganism cells produce a lot of daughter organisms, which are mainly fail to fix upon the carrier, and are washed out and get into the chamber wherein the first treatment stage is performed.

It is advisable that the effluent supply through **Pseudomonas fluorescens B-5040** microorganism culture immobilized on a solid carrier be performed within the electric field of intensity between 0.5 to 2.0 V/cm. In this case it is increased the resistance of microorganism culture against the osmotic impacts occurring when effluent flows are supplied at a different rates, which case is not rare under production conditions. As a solid carrier there could be used the fibrous or grained materials, or Rashig rings.

The main features and advantages of the invention will more clearly appear from the following description of the preferred embodiment and examples.

In order to purify effluent according to our invention, the microorganism culture is first

cultivated. The digestors of 5,25 and 30 litres were used therefor. Pure microorganism culture was cultivated in said digestors by successive seedings. Having been cultivated for 18 hours, the microorganism culture was supplied into an accumulating vessel. From this vessel said culture was further delivered to a chamber for mixing with effluent therein.

As microorganism culture there can be used: **Pseudomonas sp. 1; Pseudomonas aeruginosa A; Bacillus sp.** T2 as well as the bacterial association of **Pseudomonas sp.1** and **Bacillus sp.** T2 with the ratio therebetween being 59:41. **Preudomonas flueorescens** B-5040 strain may be also well suited for the purpose of the invention. Said strain was desposited in All - Union Collection of Industrial Microorganisms of "VNII Genetics Institute" on September 15, 1989. The strain was isolated from the slurry of tailings dump of Mardjambulak gold recovery plant in Uzbekistan and was cultivated on the agarized effluent of the same plant, containing 100 mg. of cyanides per one litre of effluent.

Following are the main characteristics of **Pseudomonas flueorescens** strain.

The cultural-and-morphologic properties of **Pseudomonas fluorescens** B-5040 strain: the cells of this strain are gram-negative ones of a size 2 to 2.5 x 0.4 to 0.5 mm that do not produce capsules and spores.

When being cultivated on meat-peptone agar at 30°C for 24 hours the strain produces small, non-transparent, slighly concave oval colonies with slighly fibrous edges. These colonies are dark-green, have uniform, finely-grained structure and viscous consistency. They form pigment, diffusing into the nutrient medium.

On meat-peptone broth, when shaken, the above strain produces uniform turbidity. In a standing stage it does not form film.

On agar-containing mineral medium (30°C, 24 hour), including the following components (g/l): K2HPO4 - 1; MgSO4 - 0.3; NaCl -0.1; Na2CO3 - 0.5; peptone - 05;

glucose 2.0; NaCN -0.1; Na3AsO4 0.5; agar-agar - 20.0; water - up to one litre, at pH between 9.0 to 9..5 there were produced small, semi-transparent oval colonies of flat profile, brilliant surface, wavy edges and whitish colour.

The colonies cultivated on solid and agarized medium are not clammed for a period of one month at a temperature between 2 to 4°C.

The physiological and biochemical properties of microorganism strain are as follows: **Pseudomonas fluorescens** is aerobic. It is cultivated at a temperature between 20 to 32°C, the optimal temperature being in the range between 28 to 30°C. The maximum growth rate is observed at 30°C. This culture does not grow at 42°C and grows slowly at 4.0°C. The optimal pH value is between 8.5 to 10.0. It does liquefy gelatine and does not hydrolize starch. Nitrates reduces to nitriles. This culture is catalazo-and-oxidazo positive.

As for the carbon supply, it consumes well glucose, lactose, maltose, saccarose, arabinose, mannit, tregalose, galactose, salicine, and does not assimilate dulcite; utilizes piruvate and lactate.

The microbial strain grows in the presence of 5 and 7% of NaCl. It is well stored in liophilically dryed state. By its genetic features this strain is prototrophe. According to Bergy identification manual it is determined as **Pseudomonas fluorescens** strain. It has been recognized as non-patogenic.

A sample of the microorganism **Pseudomonas fluorescens B5049** was deposited in the All-Union Collection of Industrial Microorganisms of VNIT Genetics Institute on 24 October, 1989 under Deposit No. B5040.

Affluent subjected to treatment according to the proposed process contains different concentrations of cyanides and gold. In this embodiment of the invention there was treated effluent containing between 0.032 to 0.120 g/l of cyanides and about 0.0008 g/l of gold. The affluent to be treated may also include the following components (approximate concentrations in g/l): arsenium-0.0065: sulphates-0.605; chlorides-0.184; calcium-0.012; magnesium-0.021 copper-0.006; zinc-0.039; ferrum-0.005; stibium-0.0005; silver-0.00026; rhodanides-0.056-0.063. In the water to be treated there may also be a considerable amount of substances in the disperse (suspended) state, with the ratio between the solid particles and liquid phase being 1:1 to 1:2.

The process of effluent treatment according to the invention may be carried out under the batch and continuous operation conditions.

Following is the description of batch process of water treatment.

Effluent in an amount of 14 cubic metres and microorganism culture in an amount of 0.6-10.0 g/l at the first treatment stage was supplied from accumulator into the chamber of 24 cubic metres and this mixture was agitated there by air for between 24 to 72 hours. The most preferable operation conditions at this treatment stage are the ones when **Pseudomonas fluorescens** B-5040 strain is used as microorganism culture and the agitaion of effluent and said strain is performed at a temperature between 26 to 30℃ and at pH between 7.5 to 9.0. The air used for agitating said mixture of effluent and microorganism culture was supplied at a ratio between said mixture and said air respectively 1:1 to 1:2, with the disperse particles, if any, being present in a suspended state.

At the first treatment stage the agitation may be performed within an electric field of intensity between 0.5 to 2.0 V/cm. In this case, for example, graphite electrodes are placed into the chamber, where the agitation of effluent and microorganism culture is performed. The electric field may be cyclically applied, that is, the field of intensity between 0.5 to 2.0 V/cm being produced between graphite electrodes is applied for between 30 to 60 seconds and during this period the agitation of said mixture is performed by this field effect; then the electrodes are switched off and agitation is further carried out for between 0.25 to 1.0 hour without the electric field being applied. The above cyclic treatment was performed during the whole period of agitation of the effluent and microorganism mixture at the first

treatment stage.

After the above treatment the mixture of effluent and microorganism culture was supplied to the second treatment stage into a chamber, whereinto the anion-exchange resin in an amount of 3-5 litres per one cubic metre of effluent has been previously introduced and agitation of said mixture by air was performed for between 0.5 to 3.0 hours. As an anion-exchange resins there were used the resins of gold selectivity between 0.4 to 1.2, namely the weak-based anion- exchange resins from sterene and divinylbenzene copolymer, containing 10% of divinylbenzene. Said copolymer is chloromethylated by monochrome-ether and is further aminated. As a result, bifunctional resin is produced, which contains the weak-based N(CH3)2 groups and strong-based N+(CH3)3 groups and has the gold selectivity value of 0.5.

Having completed the agitation process the anion-exchange resin was separated from water on a drainage device.

The continuous process of purifying effluent from cyanides was performed as below described.

The cultivated microorganisms were supplied from accumulator into the chamber, where mixing thereof with effluent was performed. In this chamber the agitation of said mixture was carried out as described above. Following this treatment the mixture of effluent and microorganism culture was delivered by pumping into the second chamber. At this time the non-purified water was supplied into the first chamber at a rate between about 0.25 to about 0.69 m3/hour. At the same time a fresh portion of microorganism culture was simultaneously introduced into this chamber. The process of agitation in the second camber was realized under conditions similar to those in the first chamber as described above. Having completed the agitation, the mixture of effluent and microorganism culture was successively supplied

from the second chamber into the third one, and from the first into the second chamber, with the first chamber being simultaneously filled with further portion of effluent and microorganism culture. The agitation process in all three chambers occurred under the above described conditions. The time of agitating said mixture in each of three chambers was between 8 to 24 hours. Therefore, the continuous process of purifying effluent from cyanides may be realized at least in three chambers, where the successive agitation of effluent and microorganism culture by air is performed. At least in two chambers, preferably in the first and second ones, there may be the placed graphite electrodes in order to produce the electric field. In this case, the agitation was performed by the effect of electric field. Characteristics of electric field in each of the above chambers are similar to the described above. The electric field may also be cyclically applied as specified for the batch process.

The second stage effluent treatment was carried out like that of the batch process, except for that one more chamber with anion-exchange resin may be additionally used. The above chamber is required, when the anion-exchange resin needs to be regenerated.

Prior to batch or continuous process of water treatment the effluent may be passed through **Pseudomonas fluorescens B-5040** microorganism culture immobilized upon a solid carrier. The chamber of a capacity 4000 litres is first charged with a solid carrier. The chamber may be fully filled with a carrier or be half empty, but in any case , the carrier must be uniformly distributed within the chamber. The main requirement to the materials to be used as a carrier is their resistance to cyanides and other agressive reagents to be found in effluent, as well as their biological inertness. The fibrous materials like natural and synthetic fibres, the disperse particles such as silicagel, ion-exchange resin, glass and polyvinyl crumb, etc., as well as Rashig rings are being used as solid carrier.

The microorganism culture is further cultivated as disclosed above. The chamber was

previously charged with fresh nutrient medium for microorganism cultivating, and **Pseudomonas fluorescens B-5040** microorganism culture was supplied thereinto. By means of aerolift pump the microorganism culture was supplied from the bottom part of the chamber to the top one, and from above this culture continuosly sprinkled the solid carrier to be found in this chamber.

Having been fixed the microorganism culture upon a solid carrier the aerolift pump was switched off. After that the effluent was further supplied to the first treatment stage through said microorganism cells immobilized on a solid carrier. The treatment was performed as previously described.

The purified water was tested to evaluate the cyanide concentration. The amount of extracted gold was also determined. The concentration of cyanides was measured by photometric technique using pyridine and barbituric asid. The amount of gold was determined by spectro-photometric technique.

The main features and advantages of the invention will be futher illustrated by the following examples.

Example 1

The purification of effluent from cyanides according to present invention was practiced as described below.

Batch Treatment Process

The microorganism culture was first cultivated as specified above. The culture of bacterial association BA-1 was used for practising this invention. The effluent, containing 0.032 g/l of cyanides and 0.0002 g/l of gold was subjected to treatment. The ratio between the solid particles being present in the water and the liquid phase was 1:2. At the first treatment

At the first treatment stage the effluent in an amount 14000 litres and microorganism culture in an amount of 6000 litres (concentration 0,8 g/l) were supplied into the chamber and agitation of said mixture of effluent and microorganism culture was performed by air for 72 hours. The air was supplied under the pressure 0.25 MPa with the ratio of mixture of effluent and microorganism culture to air being respectively 1:1. The temperature of said mixture was 28 C and pH 8.5.

At the second treatment stage the mixture of effluent and microorganism culture was delivered into the chamber, whereinto 60 litres of anion-exchange resin was previously introduced. The resin used was the weak-based anion-exchange resin of gold selectivity 1.2. The agitation was performed by means of air for 0.5 hours at a temperature 25 C..

Having accomplished the treatment in this chamber, the resin was separated from water on the drainage device.

There was determined the concertration of cyanides in purified water as well as the amount of gold to be extracted from effluent. The obtained results are presented in Table 1.

Example 2

Process for purifying effluent from cyanides is performed as described below.

Continuous Process of Water Treatment

The microorganism culture was cultivated as stated above. **Bacillus sp.** 12 strain wasused as microorganism culture. Effluent like in example 1 was subjected to treatment. These effluent, however, did not contain the disperse phase.

At the first treatment stage the effluent in an amount of 14000 litres was introduced into the chamber simultaneously with adding said microorganism culture thereinto in an amount of 6000 litres (concentration 1.0 g/l) and agitation of mixture of effluent and microorganism culture for about 24 hours was performed by air supplied under the pressure of 0.25 MPa, with the ratio of said mixture to air being respectively 1:2. The temperature of effluent and microorganism culture

constituted 30 C and pH 8.0.

Following treatment in the first chamber said mixture of effluent and microorganism culture was supplied to the second chamber and fresh portion of 14000 litres of effluent and 6000 litres of microorganism culture replaced the above mixture in the first chamber. The newly supplied mixture in the first chamber and the mixture of effluents and microorganism culture in the second chamber were agitated by air for 24 hours under the above specified conditions. Thereafter the mixture of effluent and microorganism culture was further delivered to the third chamber; from the first chamber said mixture was directed to the second one and a new portion of effluent (14,000 l) and microorganism culture (6000 l) was supplied into the first chamber. Said mixture was agitated by air in all three chambers under the above stated conditions.

Following said treatment the mixture of effluent and microorganism culture from the third chamber was supplied to the second treatment stage into the chamber, whereinto the anion-exchange resin in an amount of 100 litres (5 l/m3 of effluent) was previously introduced.

The anion-exchange resin used is the same as in example 1.

The agitation of said mixture in this chamber was carried out by means of air for 1.5 hours at a temperature 25 C. At the same time, there was performed the agitation of said mixture in the third chamber, whereinto the mixture of effluent and microorganism culture from the second chamber was supplied. The agitation was also simultaneously performed in the second chamber, whereinto the portion of said mixture from the first chamber was charged, as well as in the first chamber, to which a fresh portion of effluent and microorganism culture was added at a rate of 0.27 m3/h.

Having treated the effluent and microorganism culture in the chamber with

anion-exchange resin, said resin was separated therefrom on a drainage device.

There was determined the concentration of cyanides in treated water as well as the amount of the extracted gold. The results are presented in Table 1.

Example 3

Process for purifying effluent from cyanides according to the invention was practised as hereafter described.

The microorganism culture was first cultivated as previously specified. **Pseudomonas fluorescens B-5040** strain was used as microorganism culture. Effluent like this in example 1 was subjected to treatment.

The treatment process was practised as described in example 2. Conditions of purifying the mixture of effluent and microorganism culture in all three chambers were identical: time of agitation - 18.5 hours, pH - 8.5, temperature of effluent and microorganism culture - 30C.

The second stage treatment was similar to that in example 2, with the anion-exchange resin being used according to example 1.

The concentration of cyanides in treated water and the amount of extracted gold were determined and presented in Table 1.

Example 4

Process of purifying effluent from cyanides was performed as specified below.

The microorganism culture was cultivated as previously disclosed. **Pseudomonas fluorescens B-5040** was used as microorganism culture. The effluent, containing 0.086 g/l of cyanides and 0.00014 g/l of gold was subjected to tretment. The ratio between the solids being present in the water and the liquid phase was 1:2.

The process of purifying effluent at the first treatment stage was performed as described in example 2. However, the agitation of mixture in the first and second chambers in this case

was conducted by electric field of intensity 1.0 V/cm. In each of said three chambers the agitation of effluent and microorganism culture was carried out for 8 hours, at pH 8.3 and at a temperature of effluent and microorganism culture 26°C.

The second stage treatment was practised identically to example 2, with the anion-exchange resin being used according to example 1.

The data on cyanide concentration in treated water as well as on the amount of extracted gold is given in Table 1.

Example 5

Process of purifying effluent from cyanides according to the invention was performed as described below.

The microorganism culture **Pseudomonas fluorescens** B-5040 was first cultivated.

The effluent, containing 0.120 g/l of cyanides and 0.08 g/l of gold was subjected to treatment. The ratio of solid particles to be present in the water to the liquid phase constituted 1:2.

The first stage treatment was performed as described in example 4. The agitation of mixture in the first and second chambers was carried out by electric field of intensity2.0 V/cm. In each of three chambers the mixture of effluent and microorganism culture was agitated for 10 hours, at pH 9.0 and at a temperature of said mixture 30°C.

The second stage treatment was practised according to example 1. The weak-based anion-exchange resin of selectivity 0.4 was used for water treatment. The concertration of cyanides in treated water and the amount of extracted gold were tested. The results are presented in Table 1.

Example 6

Process of purifying water from cyanides in accordance with the invention was performed as disclosed below.

The microorganism strain **Pseudomonas fluorescens** B-5040 was cultivated as previously disclosed.

Effluent, identical to that, described in example 4 was subjected to treatment. At the first treatment stage the effluent in an amount 1400 litres and microorganism culture in an amount 600 litres (concentration 0,6 g/l) were agitated by air between 24-36 hours, at pH 7.5 and at a temperature of effluent and microorganism culture 30°C. During the whole period of agitation the above mixture was subjected to cyclic action of electric field, that is, for 45 seconds the mixture was agitated by electric field of intensity 0.5 V/cm and for further 1.0 hour the agitation was performed without this field being applied.

The second stage treatment was made in accordance with example1. The anion-exchange resin like in example 1 was used for water treatment.

The concentration of cyanides in treated water, as well as the amount of the extracted gold were measured, and the obtained results are presented in Table 1.

Example 7

Process of purifying cyanide-containing effluent in accordance with the invention was practised as specifield below.

Microorganism culture **Pseudomonas fluorescens** B-5040 was first cultivated as specifield above. Effluent, containing 0.120 g/l of cyanides, 0.63 g/l rhodanides, 0.0008 g/l gold and 0.0036 silver was subjected to treatment.

Effluent was purifield according to example 4, with the exception that the period of agitating said mixture in each chamber constituted 14 hours.

The strong-based resin of gold selectivity 0.5, containing N+(CH3)3 groups was used at the second treatment stage.

After treatment there was tested the concentration of cyanides in purifield water as well as the amount of extracted gold and silver. The results are given in Table 1.

Example 8

Process for purifying effluent according to the invention was practised as hereafter described.

The microorganism culture was cultivated as previously disclosed. The chamber of 4000 l was charged with anide fibres, microorganism culture **Pseudomonas fluorescens** in an amount 1500 l and fresh nutrient medium for culturing microorganisms in an amount 2500 l. The immobilization of said mocroorganism culture upon the anide fibres was made as previously specifield. Prior to being supplied to the first treatment stage the effluent was passed through microorganism culture immobilized upon the anide fibres. The further treatment process was realized.

The concentration of cyanides in treated water and the amount of the extracted gold were determined, and the results are presented in Table 1.

Example 9

Process for purifying effluent from cyanides was practised as hereafter specified.

The microorganism culture was first cultivated as previously disclosed. The chamber of a capacity of 4000 litres was charged with the anide fibres, Pseudomonas fluorescens B-

5040 microorganism culture and nutrient medium for microorganism culturing. The immobilization of said culture on the anide fibres was performed as specified in example 8. The electric field of intensity 0.5 V/cm was produced in said chamber , and effluent was supplied to the first treatment stage through said microorganism culture, which was under the effect of above said electric field.

The further process of water treatment was performed as described in example 1.

There was determined the concentration of cyanides in treated water and the amount of the extracted gold.

The obtained results are summarized in Table 1.

Example 10

Process for purifying effluent according to the invention was performed as hereafter described.

The microorganism culture was first cultivated as previously specified. The chamber of 4000 litres was charged with polyvinyl crumb of a grain size between 0.8 to 1.2 mm, **Pseudomonas fluorescens B-5040** microorganism culture and nutrient medium for cultivating microorganisms. The immobilization of said microorganism culture on the polyvinyl crumb was made as in example 8. The electric field of the intensity 2.0 V/cm was additionally produced in said chamber , and the effluent was supplied to the first treatment stage through said microorganism culture, which was under the effect of said electric field.

The process was further performed as disclosed in example 1.

There was determined the concentration of cyanides in treated water and the amount of the extracted gold.

The obtained results are given in Table 1.

Example 11 (Comparative)

Process of effluent purification was realized as follows below.

Microorganism culture as described in example 4 was used for the purpose of the invention.

Effluent, containing 0.083 g/l of cyanides and 0.0002 g/l of gold was purifield according to the invention. The ratio of solid particles to be found in the water to the liqud phase was 1:2.

The first treatment stage was performed as in example 4. The agitation of effluent and microorganism culture was carried out under the action of electric field of intensity 0.3 V/cm. The time of effluent treatment in three chambers equalled 58 hours.

Second stage treatment was performed similar to example 1. The concertration of cyanides in treated water, as well as the amount of extracted gold were determined after effluent treatment. The obtained data are presented in Table 1.

Example 12 (Comparative)

Process of effluent treatment was practised in accordance with the described below.

The microorganism culture according to example 4 was used in this case. Effluent having the composition as specifield in example 5 was subjected to treatment.

The first treatment stage was the same as in example 4. Effluent and microorganism culture were agitated by electric field of intensity 3.08 V/cm. Duration of treatment in three chambers was 32 hours.

The second stage treatment was made as in example 1.

The decrease in electric field intensity below the specified value (example 11) results in a considerable increase in a period of agitating the mixture of effluent and microorganism culture required to achieve the results equal to those in example 4. So, in example 4 the time of agitation in each of three chambers at the first treatment stage was 24 hours, while in example 8 the period of agitation constituted 58 hours. The electric field of above intensity (example 8) appears to be non-effective in effluent treatment process. The increase of electric field intensity above the specified limit range (example 12) reduces the efficiency of effluent treatment and decreases the amount of extracted gold.

The reduction of temperature of the effluent and microorganism culture to 20°C also adversively affects the quality of water treatment (example 13).

Exclusion of either stage from the process for purifying effluent from cyanides does not permit to efficiently remove cyanides from water and at the same time to provide the required degree of extracting noble metals to be found in the water (examples 14-15). At the same time, one can clearly see from the above examples that the first stage use of microorganism culture and the second-stage application of anion-exchange resin improves both the cyanide destruction and gold recovery.

It should be understood that this disclosure refers only to several specific examples of practising the invention. Other modifications will appear to those skilled in art within the scope of this invention. For full definition of the scope of the invention, reference is to be made to the attached claims.

TABLE 1

Characteristics	Examples according to the invention										Comparative examples					Romanian patent 69528
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	
Cyanide concentration in treated effluent, g/l.10^-4	7	9,5	1	1	1	1,5	1	6,8	7,6	2,4	1	14	5	3	8	10
Rhodanide concentration in treated effluent, g/l .10^-4	-	-	-	-	-	-	1	-	-	-	-	-	-	-	-	-
Gold extraction, %	90	87	90	85	72	85	87	87	90	90	85	60	83	-	70	-
Silver extraction, %	-	-	-	-	-	-	92	-	-	-	-	-	-	-	-	-

The concertration of cyanides in treated effluent, as well as the amount of extracted gold were measured after the treatment. The results are summarized in Table 1.

Example 13 (Comparative)

Process of purifying cyanide-containing effluent was performed in accordance with specifield below.

The microorganism culture as in example 1 was used for practising the invention.

Effluent of composition similar to that of example 4 was subjected to treatment.

The first treatment stage was performed according to example 4.

The agitation of effluent and microorganism culture was carried out by the action of electric field of intensity 2.0 V/cm for 75 hours at a temperature 20 °C.

The second stage treatment was practised as in example 2.

The concentration of cyanides in treated water, as well as the amount of extracted gold were determined, and the obtained data are presented in Table 1.

Example 14 (Comparative)

Following is the description of effluent treatment process according to the invention.

The microorganism culture as in example 3 was used to attain the objects of the invention.

Effluent of composition similar to that of example 1 was subjected to purification.

The first treatment stage was practised according to example 1.

In this example, there was no second stage treatment of effluent.

The concertration of cyanides in the water after the first treatment stage, as well as the amount of extracted gold were determined after the treatment. The obtained results are given in Table 1.

Example 15 (Comparative)

Process of removing cyanides from effluent was performed as hereafter described.

The microorganism culture as specifield in example 3 was used for practising the invention.

Effluent of composition like in example 1 was subjected to treatment.

The process of purifying effluent according to this example included only the second stage of treatment, as described in example 4. After the treatment process there was determined the concertration of cyanides in purifield water, as well as the amount of extracted gold. The obtained results are presented in Table 1.

The results of purifying effluent from cyanides in accordance with Romania patent Nº69528 are also included into the Table 1.

As it is clearly seen from Table 1, the process for purifying effluent according to present invention (examples 1-10) allows to efficiently purify cyanide-containing effluent and at the same time to recover noble metals therefrom. The best results in cyanide destruction were achieved when using **Pseudomonas fluorescens B-5040** strain as microorganiam culture (examples 3-7).

As stated above, the application of electric field intensifies the vital activity of microorganisms and consequently, promotes more efficient purification of cyanide-containing effluent within a shorter period of time (examples 4-6). In addition, the process enables the effluent containing rhodanides, as well as gold and silver to be also effectively treated (example 7).

The high parameters of purifying effluent from cyanides are also achieved when first passing effluent through the microorganism culture immobilized on a solid carrier (examples 8-10).

CLAIM:

1. A process for purifying cyanide-containing effluent, consisting in that the purification of effluent is performed in two stages:

at the first treatment stage the effluent and a microorganism culture in an amount between 0.6 to 1.0 g/l are introduced into a chamber and agitation of said mixture is carried out for between 24 to 72 hours;

at the second treatment stage said mixture of effluent and microorganism culture is further supplied into a second chamber, whereinto an anion-exchange resin of gold selectivity between 0.4 to 1.2, in an amount between 3.0 to 5.0 litres per one cubic metre of said mixture is added;

and the resulting mixture is agitated by and with air for between 0.5 to 3.0 hours.

2. The process for purifying cyanide-containing effluent as claimed in claim 1, characterized in that the agitation of said mixture of effluent and microorganism culture at the first treatment stage is performed by air in at least two chambers, with said agitation of said mixture in each chamber being carried out for between 8.0 to 24.0 hours.

3. The process for purifying cyanide-containing effluent as claimed in claim 1, characterized in that the **Pseudomonas fluorescens** B-5040 strain is used as microorganism culture, and agitation of said mixture is performed at a temperature between 26 to 30°C.

4. The process for purifying cyanide-containing effluent as claimed in claim 1, characterized in that an electric field of a intensity between 0.5 to 2.0 V/cm is produced at the first treatment stage in said chamber where the agitation of said mixture of effluent and microorganism culture is carried out.

5. The process for purifying cyanide-containing effluent as claimed in claim 2,

characterized in that an electric field of intensity between 0.5 to 2.0 V/cm is produced at the first treatment stage in at least two chambers where the agitation of a mixture of effluent and microorganism culture is carried out.

6. The process for purifying cyanide-containing effluent as claimed in claim 1, characterized in that an electric field of intensity between 0.5 to 2.0 V/cm is produced at the first treatment stage in said chamber where the agitation of a mixture of effluent and microorganism culture is carried out, and the agitation of said mixture for between 30 to 60 seconds is performed by said electric field, followed by further agitation of said mixture by other means for another 0.25-1.0 hour without said electric field being applied, with such alternation of agitation with said electric field and without said electric field being practised for the whole period of agitating said effluent and microorganism culture.

7. The process for purifying effluent from cyanides as claimed in claim 2, characterized in that an electric field of intensity 0.5 to 2.0 V/cm is produced at the first treatment stage in at least two chambers, where the agitation of a mixture of effluent and microorganism culture is carried out, and wherein the agitation of said mixture for between 30 to 60 seconds is performed by said electric field followed by further agitation of said mixture by other means for another 0.25-1.0 hour without said electric field being applied, with such alternation of agitation with said electric field and without said electric field being practised for substantially the whole period of agitating said mixture of effluent and microorganism culture in each of these chambers.

8. The process for purifying cyanide-containing effluent as claimed in claim 1, characterized in that the agitation of said mixture of effluent and microorganism culture is performed by air at a ratio of said mixture of effluent and microorganism culture to air

in the range 1:1 to 1:2.

9. The process for purifying cyanide-containing effluent as claimed in claim 1, characterized in that the anion-exchange resin is a weak-based anion-exchange resin from a styrene and divinylbenzene copolymer, including 10% of divinylbenzene, and containing the weak-based N(CH3)2 groups and strong-based N+(CH3)3 groups and having a gold selectivity value of 1.2.

10. The process for purifying cyanide-containing effluent as claimed in claim 1, characterized in that the anion-exchange resin is from a styrene and divinylbenzene copolymer having 10% of divinylbenzene, and containing strong-based N+(CH3)3 groups and having a gold selectivity value of 0.5.

11. The process for purifying effluent from cyanide-containing effluent as claimed in claimed 1, wherein prior to being supplied to the first treatment stage the effluent is passed through a **pseudomonas fluorescens** B-5040 microorganism culture immobilized on a solid carrier.

12. The process for purifying effluent from cyanide-containing effluent as claimed in claim 11characterized in that the effluent is passed through Pseudomonas fluorescens B-5040 microorganism culture immobilized on a solid carrier under the effect on an electric field of intensity between 0.5 to 2.0 V/cm.

13. The process for purifying effluent from cyanide-containing effluent as claimed in claim 11 or 12, characterized in the solid carrier is a fibrous or grained material, or Rashig rings.

14. A process according to claim 1 substantially as herein described with reference to any one of the illustrative Examples.

INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/GB 96/02537

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C02F3/02 C02F9/00 C02F1/42 C02F1/48

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO,A,93 16962 (958075 ONTARIO INC CARRYING ON) 2 September 1993 see page 1, line 17 - page 2, line 5 see page 4, line 15 - page 5, line 20 see page 8, line 1 - page 10, line 5 ---	1,2,4,7, 11
A	US,A,5 169 532 (WHITLOCK) 8 December 1992 see column 2, line 48 - line 64 see column 4, line 42 - line 63 see column 5, line 12 - line 32 ---	1-3,11, 13
A	US,A,3 660 278 (MIMURA ET AL) 2 May 1972 see column 3, line 9 - line 38 --- -/--	1-3

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
10 February 1997	27.02.97
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016	Authorized officer Ruppert, G

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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A	HYDROMETALLURGY, vol. 33, no. 1/02, 1 June 1993, pages 43-58, XP000415599 RIVEROS P A: "SELECTIVITY ASPECTS OF THE EXTRACTION OF GOLD FROM CYANIDE SOLUTIONS WITH ION EXCHANGE RESINS" see page 44, paragraph 2; figure 6 see page 56, paragraph 1 - page 57, paragraph 2 see tables 1,3-6 ---	1,9,10
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INTERNATIONAL SEARCH REPORT

.nformation on patent family members

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PCT/GB 96/02537

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